FINAL REPORT

U.S. DOT
Pipeline and Hazardous Materials Safety Administration

Competitive Academic Agreement Program

Mitigating external corrosion of pipelines through nano-modified cement-based coatings

The Trustees of Columbia University in the City of New York

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PROJECT SUMMARY

With the aim to mitigate external corrosion of pipelines, the proposed work performed the characterization necessary to explore the feasibility of engineering a cement-based coating material that exhibits superior sealing properties and ease of implementation. The advantage of cement-based coatings over other types is that they can be designed to possess mechanical properties to provide structural stability for the pipeline, as well as offset buoyancy. To attain the properties desired for pipeline coating, the approach involved utilization of nanomaterials and supplementary cementitious materials (SCMs), investigation of advanced processing techniques, and characterization of key properties relevant to coating applications, i.e. mechanical properties, permeability, and rheology.

Due to variations in loading that can occur in offshore conditions, the coating material must possess sufficient mechanical properties. The potential of CNTs to enhance mechanical properties, i.e. tensile and compressive strength, was investigated. If water penetrates through the coating material, either as a result of high porosity or cracking, and gains access to the space between the coating and pipeline surface, the pipeline becomes susceptible to water exposure and subsequently vulnerable to external corrosion. Therefore the coating material must exhibit low permeability. The potential of nanomaterials, fly ash and blast-furnace slag in combination to refine the pore structure and develop a highly percolated network were explored via a direct and indirect method of porosity. And from a practical standpoint, it is important that the coating can be applied efficiently and effectively during application. Therefore a highly-purified, nano-sized attapulgite clay will be explored to enhance key rheological properties in order to facilitate the process of applying a uniform layer of coating to the pipeline during production.

Results of the work indicate that although the nanoclays were utilized primarily as a rheological modifier, they had an enhancing effect on the mechanical properties that were comparable to or greater than the CNTs. This was attributed to improved suspension stability and seeding effects achieved through the nanoclays, and the difficulty in achieving effective dispersion of the CNTs. Replacement of cement content with SCMs by up to 50% while achieving comparable mechanical properties as the control was possible. Although the findings indicated that SCMs, CNTs, and attapulgite clays were found to improve permeability, the effect was not significant. Therefore cement-based coatings as a stand alone solution for pipelines is likely not feasible, and instead requires a dual layer with a polymer-based base coating. Rheological characterization indicated that the attapulgite clays achieved a balance between high flowability during casting and high stiffening at rest that would be beneficial for the coating process. This in combination with the improvement in mechanical properties and permeability suggests that attapulgite clays may be sufficient for cement-based pipeline coatings, not requiring CNTs. This can be beneficial as this simplies the system to avoid admixture incompatibility. Further, attapulgite clays are readily dispersible, making processing less costly and more efficient.

1 MATERIALS

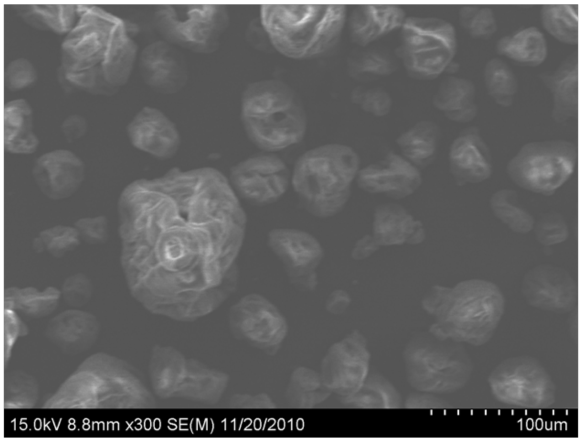
All mixes used Type I Portland Cement and tap water. The cement had a Blaine fineness of 420 m^2/kg and its chemical composition is shown in Table 1. All fine aggregates were seized to attain a maximum grain size of 1.18 mm.

Table 1 - Chemical composition of Type I Portland Cement and Type F Fly Ash.

Chemical Oxide	**Type I Cement (%)**	**Type F Fly Ash (%)**
SiO2	19.22	47.2
Al2O3	4.98	23.4
Fe2O3	3.42	16.6
CaO	62.42	4
MgO	3.87	-
SO3	2.72	1.3
Free Lime	0.95	-
Loss on ignition	2.62	2.1
CO2	1.9	-

1.1 ATTAPULGITE NANOCLAYS

A commercially available, highly purified form of mineral attapulgite, or palygorskite, (ACTIGEL 208, Active Minerals) was the clay chosen for this project. They are chemically exfoliated from bulk attapulgite to remove impurities such as smectite, bentonite, and other swelling clays, making them effective rheological modifiers. They were incorporated into the mixes primarily to tailor the "fresh-state" properties, i.e. before setting, and facilitate the coating application process.



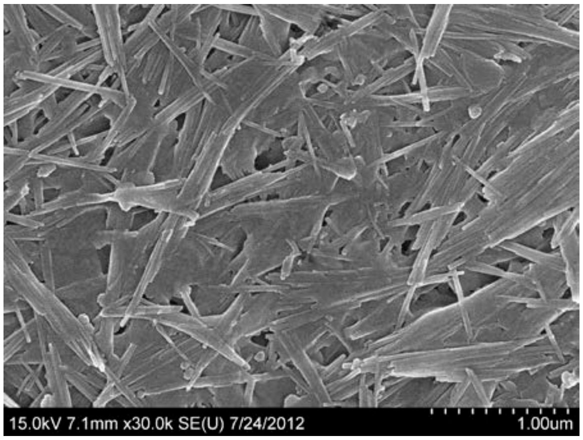


Figure 1 - Purified attapulgite clays in the agglomerate (left) and dispersed (right) state.

Figure 1 shows scattering electron microscopy (SEM) images of the clays in two states. The left image shows the clays in the as-received, dry state – they are noticeably agglomerated and in the micron-size. The right image shows the clays after they have been dispersed and become rod-like. The manufacturer reports that they are 1.75 μm in average length and 3 nm in average diameter. Therefore they can be considered as rod-like nanoclays. They are highly hydrophilic, so readily dispersible in water. This has positive implications for practical applications, where they do not require any additional processing to uniformly disperse in concrete mixes due to the high shear introduced locally by the presence of aggregates. For nanomaterials dispersion is necessary to achieve, otherwise they will not be effective. Therefore in our tests, to ensure sufficient dispersion the clays were always pre-blended in water in a Waring blender and incorporated into the mix as a suspension.

1.2 CARBON NANOTUBES (CNTs)

CNTs exhibit superior mechanical properties (Young's modulus up to 1 TPa and tensile strength up to 100 GPa) along with extremely high aspect ratios. Therefore they can be expected to enhance the properties of cement composites through various effects, including seeding, filler and reinforcing. Specifically in this study, their effect on the mechanical properties and permeability were investigated. Industrial grade multi-walled carbon nanotubes (MWCNTs) with 90% purity were selected for the study, considering the viability of scaling up for application.

As aforementioned, for the CNTs to be effective, they must be highly dispersed. Unlike the attapulgite nanoclays, CNTs are not readily dispersible. Due to high attractive van der Waals forces between CNTs, considerably high specific surface area, and high aspect ratio, they tend to aggregate. Therefore dispersion was important to consider prior to incorporating into cement composite mixes. CNTs in two forms were acquired for the study – aqueous dispersion form and dry form. To determine which form to use for the remainder of the study, their effect on modulus of rupture were compared.

1.2.1 FLEXURAL STRENGTH TEST

Flexural strength tests were performed on an Instron 5984 34k Universal Testing Machine. The standard Third-Point Loading method (ASTM C78/C78M–10) was applied to test flexural strength. Maximum applied load (P), span length (L), average width of specimen (b) and average depth of specimen (d) were recorded and modulus of rupture (R) was calculated using the following equation:

$$\mathrm{R} = \frac{PL}{bd^2}$$

The samples for flexural strength tests were cement mortars with a water-to-cement (w/c) ratio of 0.5 and sand-to-cement ratio of 2. Mixes were prepared in a medium upright planetary mixer as follows:

1) Cement and sand were dry mixed for 1 min at low speed (139 rpm).
2) CNTs and mixing water were added, then mixed for 1 min at low speed (139 rpm).
3) The sides of the mixing bowl were scraped, then mixed for 8 min at medium speed (285 rpm).

Samples were cast in 1” x 1” x 12” prism molds. After 1 day, they were demolded and cured in water for 7 or 28 days. Then, they were cut into 1” x 1” x 4” prisms for testing.

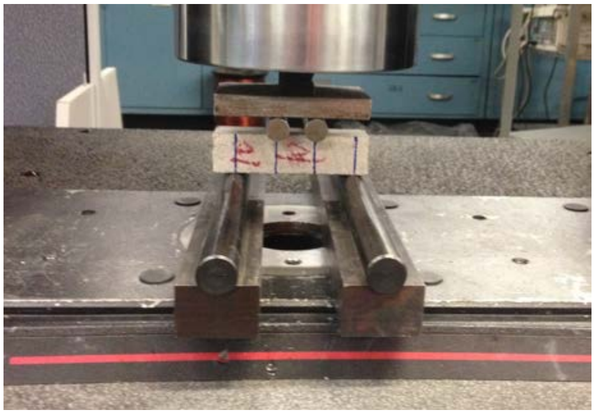


Figure 2 - Flexural strength test setup.

1.2.2 AQUEOUS DISPERSION FORM

The MWCNTs in aqueous dispersion form (AQUACTL AQ0302, Nanocyl) were composed of 3% MWCNT, < 5% surfactant, and > 90% water (by weight). The aqueous dispersion was combined with the mixing water and stirred, then added to the mix in Step 2 of the mixing protocol. MWCNT additions in the cement mortars were 0.01, 0.02 and 0.03% by mass of cement. The results of the flexural strengh tests are shown in Figure 3. It was found that the MWCNTS in aqueous form led to a decline in flexural strength. This may be attributed to the relatively high dose of surfactant the MWCNTs were treated with, which may have adversely affected strength gain.

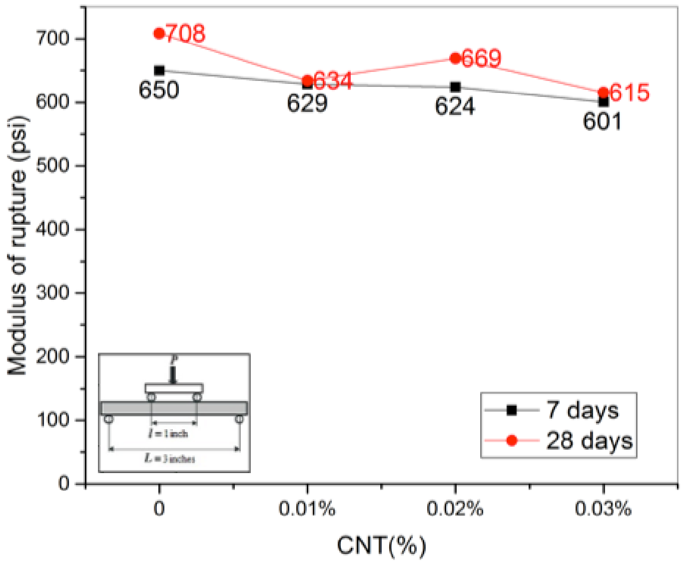


Figure 3 - Modulus of rupture of cement mortars reinforced with MWCNTs in aqueous dispersion form (as-received).

1.2.3 DRY FORM

The MWCNTs in dry form (NC7000, Nanocyl) were 9.5 nm in average diameter and 1.5 µm in average length, according to the manufacturer. (The MWCNTs tested and discussed in the previous section were the same raw materials in the pre-dispersed form.) Since they were received in dry form, it was necessary to disperse them in the lab. To do so, they were combined with water and a polycarboxylate-based superplasticizer at a surfactant-to-CNT weight ratio of 5. The mixture was then ultrasonicated in a high intensity ultrasonic processor with a cylindrical tip, operating at a constant 40% amplitude for 1 hour. The container was kept in an ice bath throughout the sonication process to avoid evaporation of the water. The resulting suspension was added to the mix in Step 2 of the mixing protocol. MWCNT additions in the cement mortars were 0.01, 0.03 and 0.05% by mass of cement. The results are shown in Figure 4. With increasing addition of MWCNTs, there was an increase in flexural strength.

The contrast between the effect of the MWCNTs in aqueous disperse form versus dry form on flexural strength may be attributed to the fact that the surfactant used to disperse the dry MWCNTs in our lab is an admixture commonly used in concrete. Therefore, they are designed to not have any adverse effects on the material. On the other hand, it is unknown what surfactant type the manufacturer used to pre-disperse the MWCNTs in the acqueous disperse form.

Based on these preliminary findings, the MWCNT in the dry form (as-received) was selected for the remainder of the study. And to ensure dispersion, they were treated with polycarboxylate-based superplasticizer and sonicated prior to adding to the mixes.

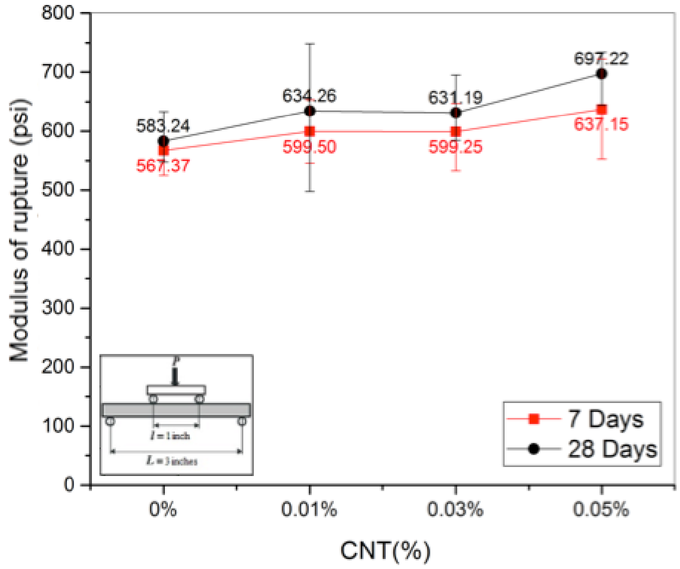


Figure 4 - Modulus of rupture of cement mortars reinforced with MWCNTs in dry form (as-received).

1.3 SUPPLEMENTARY CEMENTITIOUS MATERIALS

Supplementary cementitious materials (SCMs) were incoporated into mixes by replacement of cement. This was with the aim to refine the pore structure of the material and to reduce cement content. The SCMs that were investigated in this study were Type F Fly Ash (Separation Technologies, Inc.) and Grade 120 Blast Furnace Slag (Lafarge). The chemical composition of the fly ash is presented in Table 1.

To determine suitable proportioning of the SCMs and cement, preliminary testing on the effect of cement replacement with different amounts of fly ash and blast furnace slag (ranging from 0 to 50%) were performed. The results of 7 and 28 day compressive strength of ternary mortars are shown in Figure 5. The compressive strength of 100% cement mortar at 28 days is shown as the blue dotted line for comparative purposes. As expected, fly ash led to a strength reduction due to delayed pozzolanic reaction while slag had an enhancing effect due to increased reactivity. The goal is to achieve comparable performance as the control mix with 100% cement content while replacing as much of the cement with SCMs. It is shown at 28 days that this can be achieved at around 50% cement, 25% fly ash, and 25% slag. Therefore, this mix design was selected for the remainder of the study.

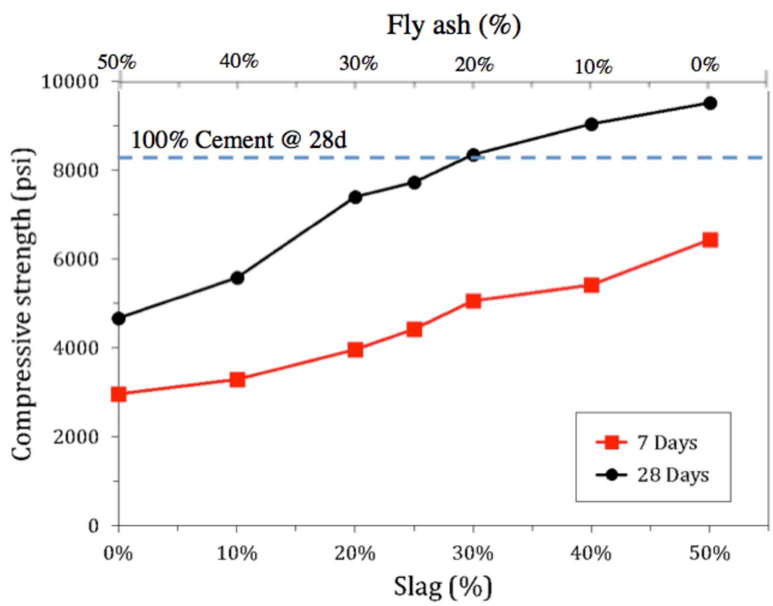


Figure 5 - Compressive strength results of ternary cement mortars with 50% Type I Portland cement and various replacement levels (by mass) of fly ash and/or blast furnace slag.

1.4 MIX PROPORTIONS

Based on the findings presented thus far, as well as previous work by the PI, the final mix design for the paste and mortar mixes were determined. They are presented in Table 2. All cement mortars were prepared with a water-to-binder (w/b) ratio of 0.5 and sand-to-binder ratio of 2. All pastes were prepared with a w/b ratio of 0.43.

Table 2 - Mix designs.

Mix	Cement	Fly Ash	Slag	Surfactant	CNT	Attapulgite Clay
	(% by mass of total binder)			(% addition by mass of binder)		
C	100	0	0	0	0	0
C_0	100	0	0	0.05	0	0
C_CNT	100	0	0	0.05	0.01	0
C_ATT	100	0	0	0.05	0	0.3
C_CNT_ATT	100	0	0	0.05	0.01	0.3
FS_0	50	25	25	0.05	0	0
FS_CNT	50	25	25	0.05	0.01	0
FS_ATT	50	25	25	0.05	0	0.3
FS_CNT_ATT	50	25	25	0.05	0.01	0.3

2 MECHANICAL AND HARDENING PROPERTIES

2.1 COMPRESSIVE STRENGTH

Compressive strength tests were performed in an Instron 600DX 135k Universal Testing Machine on 2” x 2” x 2” cubic samples in accordance to ASTM C-109. The loading rate was 200 lb/s. Three samples per mix design were tested and the average was taken to be the representative value.

Mortar samples were prepared in a medium upright planetary mixer using the following mixing protocol:

1. Binder materials (i.e. cement, fly ash and/or slag) and sand were dry mixed for 1 min at low speed (139 rpm).
2. CNTs were added as a suspension with a portion of the mixing water, then mixed for 1 min at low speed (139 rpm).
3. Attapulgite nanoclays were added as a suspension with the remaining mixing water, then mixed for 1 min at low speed (139 rpm).
4. The sides of the mixing bowl were scraped, then mixed for 8 min at medium speed (285 rpm).

For mixes without CNTs or nanoclays, only Steps 1 and 4 were performed. When only CNT or nanoclay was added, Step 2 or 3 was performed and all of the mixing water was added with the respective suspension. Samples were cast in cubic molds, demolded after 1 day and cured in water for 7 or 28 day.

2.1.1 COMPRESSIVE STRENGTH RESULTS

The results are shown in Figure 6 and Figure 7 for the cement mortar and ternary mortar mixes, respectively. In Figure 6, it is apparent that at 7 day there are slight improvements in the compressive strength compared to the control (C_0) in all mixes. At 28 day, the increase is more marked. Compared to the control, CNTs (_CNT), attapulgite nanoclay (_ATT), and combination (_CNT_ATT) result in increases of 15, 17, and 24%, respectively. Although the attapulgite clay was added to the material as a rheological modifier, it appears that it has the potential to enhance the mechanical properties, as well. The results of the cement mortar systems show that the enhancing effect by the attapulgite clay is comparable to that of the CNTs. Further, in Figure 7 it is shown that in the ternary system with fly ash and slag, the increase in compressive strength at 28 day by the attapulgite nanoclay is more pronounced than that by the CNT.

This may be attributed to two possible mechanisms: degree of dispersion and suspension stability. As discussed in the previous section, CNTs are hydrophobic so they are challenging to disperse in cement-based suspensions, requiring the right amount of surfactant and agitation. On the other hand, clays are highly hydrophilic and readily dispersible. Although processing was carefully considered in this study and the CNTs were observed to be well-dispersed in aqueous form, they can still re-aggregate when introduced to the highly alkaline environment in cement-based systems. And any aggregation of the CNTs will result in voids in the cement matrix, which translate to flaws. CNT dispersion still remains a challenge in all composite systems. Therefore, the dispersion of the clays is likely more uniform than that of the CNTs. Second, since the clay is a rheological modifier, it can be enhancing the suspension stablity of the cement-based material. This will improve segregation resistance and reduce bleeding up until setting, which will enhance the eventual mechanical performance. These beneficial effects on suspension stability by the clays and the possible aggregation of CNTs in the cement matrix may be outweighing any filler or reinforcing effects the CNTs are having on the microstructure.

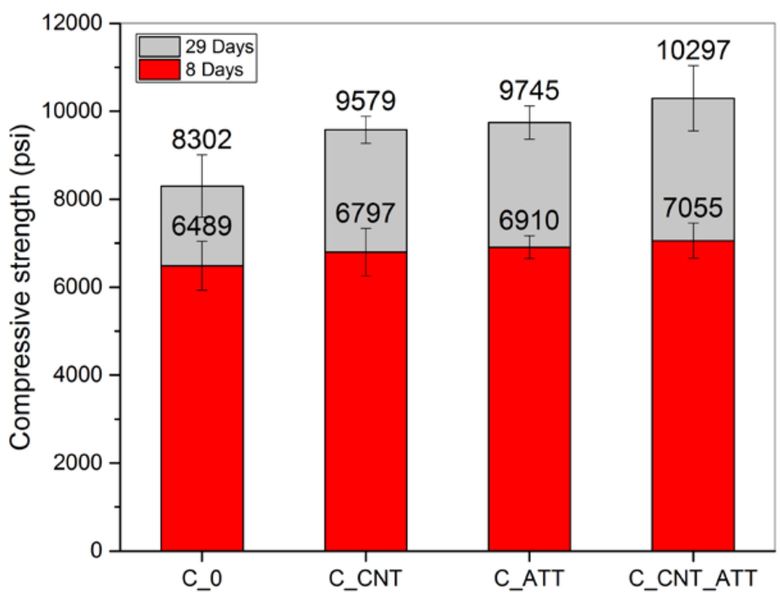


Figure 6 - Compressive strength results of cement mortar mixes.

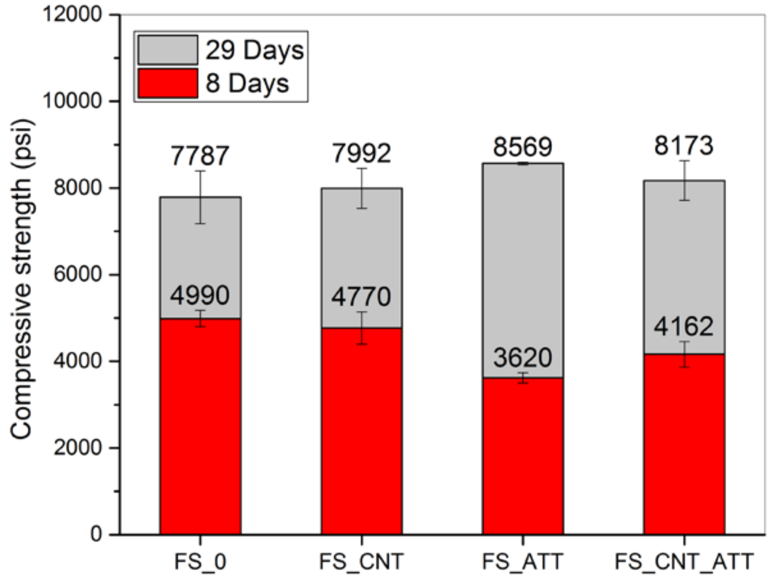


Figure 7 - Compressive strength results of ternary mortar mixes.

2.2 TENSILE STRENGTH

Direct tensile strength tests were performed in an Instron 5984 34k Universal Testing Machine on dogbone-shaped samples with a 1” x 1” tapered cross-section. The setup is shown in Figure 8. The loading rate was set at 0.20 in/min. Three samples per mix design were tested and the average was taken to be the representative value.

Paste samples were prepared in a small upright planetary mixer using the following mixing protocol:

1. Binder materials (i.e. cement, fly ash and/or slag) were dry mixed for 1 min at low speed (139 rpm).
2. CNTs were added as a suspension with a portion of the mixing water, then mixed for 1 min at low speed (139 rpm).
3. Attapulgite nanoclays were added as a suspension with the remaining mixing water, then mixed for 1 min at low speed (139 rpm).
4. The sides of the mixing bowl were scraped, then mixed for 4 min at medium speed (285 rpm).

For mixes without CNTs or nanoclays, only Steps 1 and 4 were performed. When only CNT or nanoclay was added, Step 2 or 3 was performed and all of the mixing water was added with the respective suspension. Samples were cast in dogbone shaped molds, demolded after 1 day and cured in water for 28 day.

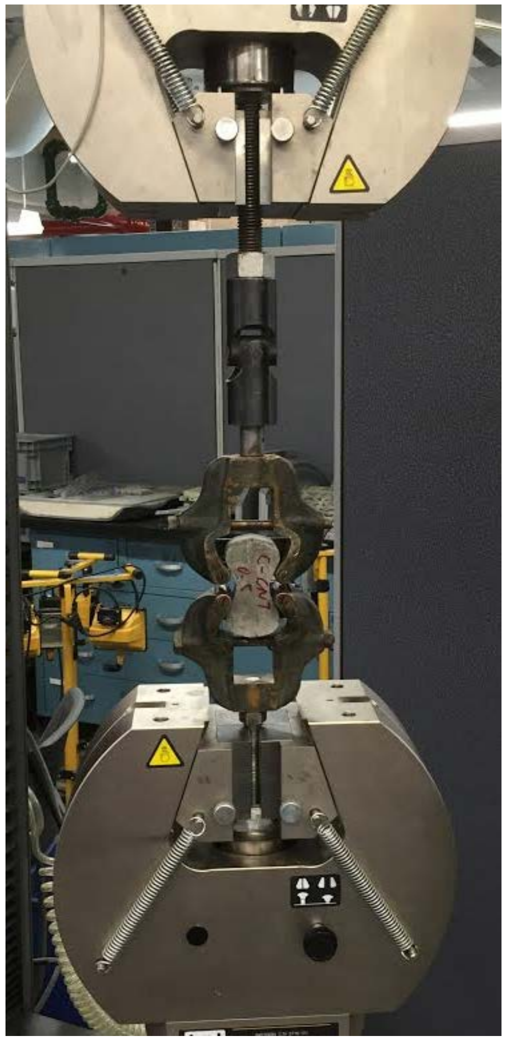


Figure 8 - Tensile strength setup.

2.2.1 TENSILE STRENGTH RESULTS

The 28-day direct tensile strength results are shown in Figure 9. The CNTs did not lead to any measurable increase in tensile strength in the cement system. However, they improved the strength in ternary systems by approximately 19%. Since fly ash particles are spherical, they have a ball-bearing effect to improve dispersion, which may be the reason why the CNTs were found to be more effective in the ternary system.

On the other hand, the attapulgite clay led to a substantial increase in tensile strength of the cement system, approximately 33% compared to the control. This, again, may be attributed to effective dispersion and improved suspension stability. However, there was no measurable effect on the ternary system. As a silicate, it is possible for the attapulgite clay to be participating in pozzolanic reaction to densify the microstructure. Pozzolanic reaction is when a pozzolan reacts with calcium hydroxide (a by-product of the main cement hydration reaction) to produce secondary calcium silicate hydrate (the main product of cement hydration). Further, as a nanomaterial, the pozzolanic reaction will occur at a more accelerated rate. In the ternary system, since it incorporates 25% slag and 25% fly ash, which are pozzolans, they compete with attapulgite clay for the same reaction. This may be the reason why a greater effect was not observed by the clays in the ternary system – there was less calcium hydroxide for the fly ash consume to sustain strength development.

Looking at the effect of combining attapulgite clay and CNTs, there does not seem to be any synergistic effects. In the ternary system, there is even a slight decrease compared to the control. It is difficult to say what the exact mechanisms are given the increasing complexity of the system, and would require further characterization.

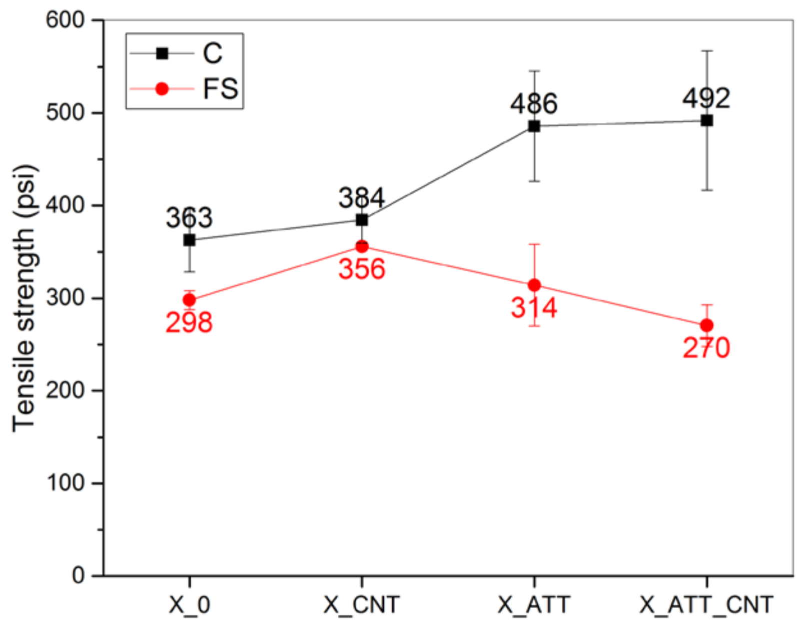


Figure 9 – 28 day direct tensile strength results.

2.3 ISOTHERMAL CALORIMETRY

Rate of hydration of cement pastes were measured through isothermal calorimetry in a TA Instruments TAM Air Isothermal Calorimeter. Cement hydration is an exothermic reaction.

Therefore monitoring the heat flow of a sample at a constant temperature provides the rate of cement hydration. Cement pastes were prepared by handstirring in a beaker. Then 5 g of paste were cast in glass vials and tested at 25°C. Three samples per mix design were tested and the average was taken to be the representative curve.

Figure 10 - TAM Air Isothermal Calorimeter

It was of interest to see how the attapulgite clay and CNTs affected the hydration kinetics, to supplement the results of mechanical characterization. The results of cement pastes with 0 and 0.01% CNT by mass of cement is shown in Figure 11. There is no measurable change by the CNTs to the hydration kinetics. Therefore, any enhancing effects by the CNTs are likely tied to filler or reinforcing effects. The results of cement pastes with 0, 0.1, 0.3 and 0.5% nanoclay addition are shown in Figure 12. It is apparent that with increasing amount of nanoclay there is higher rate of heat generation, indicating higher rate of reaction. This indicates that hydration is accelerated by the nanoclay. It is widely accepted and found that nanomaterials can have a seeding effect when incorporated into cement-based materials. The high specific surface area of nanomaterials provide additional nucleation sites for hydration products to grow. Therefore, any enhancing effects by the nanoclays can be at least partially attributed to seeding effects.

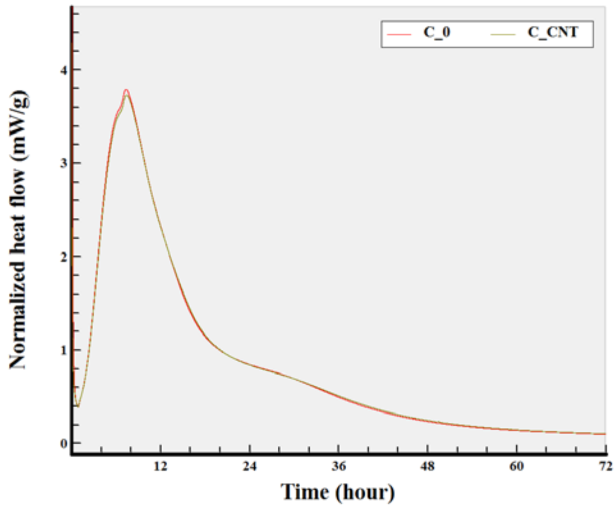


Figure 11 - Heat flow of cement paste with 0 and 0.01% CNTs.

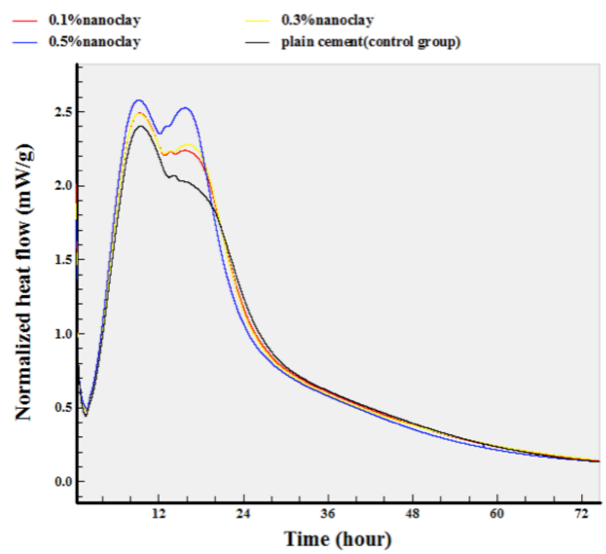


Figure 12 - Heat flow of cement paste with attapulgite clay.

3 PERMEABILITY

To gain a measure of permeability, a direct and indirect method were implemented.

3.1 POROSITY

The direct method measured porosity in accordance to ASTM C1754/C1654M on 2” x 2” x 2” cubic specimen. The exact volume of the cubic specimens were determined. The specimens were oven dried until the mass difference between two subsequent mass measurements was less than

0.5%. Then, the specimens were submerged in a water bath to determine the submerged mass, as shown in Figure 13. From there, the void content (i.e. porosity) of the specimen was calculated, as follows:

$$\text{Void Content} = \left[1 - \left(\frac{K \times (A - B)}{\rho_w \times D^2 \times L}\right)\right] \times 100$$

where:

B = submerged mass of the specimen, g [lb], and
ρ_w = density of water at temperature of the water bath, kg/m^3 [lb/ft^3].

Figure 13 – Setup to determine submerged mass.

Although this was the originally proposed technique, it was found that the resolution of the results was rather limited when it came to evaluating the effect of the nanomaterials. The results of slag replacement are shown in Figure 14. Although a decrease in porosity was capture, as expected, with increasing slag replacement, the percent change is very low. Therefore, an indirect method using electrical resistivity was implemented, and will be discussed in the following section.

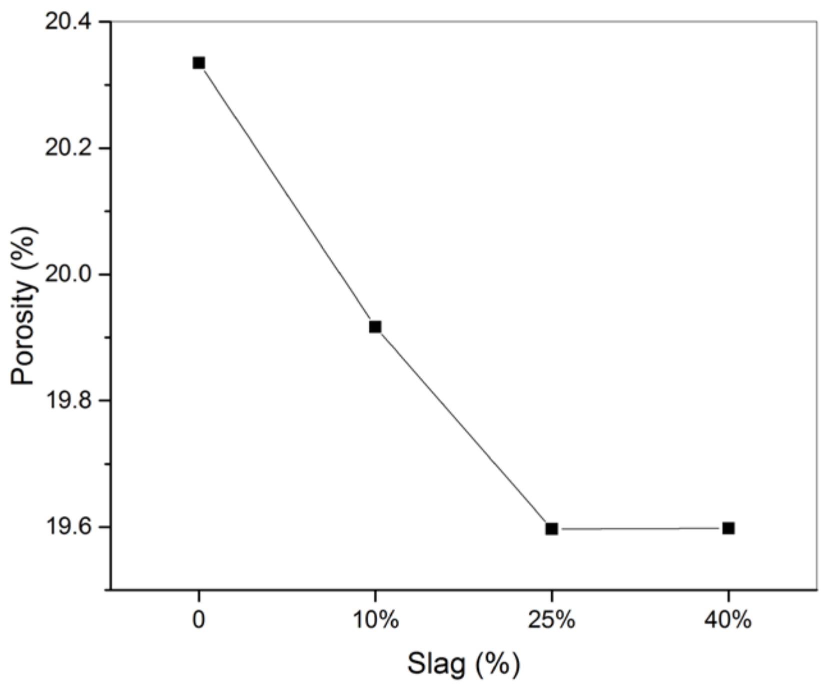


Figure 14 - Porosity results of cement mortar with slag replacement.

3.2 ELECTRICAL RESISTIVITY

Electrical conductivity tests were performed to obtain an indirect measure of permeability. 2” x 2” x 2” cubic samples were tested using an electrical resistivity meter (RCON, Giatec), the schematic of which is shown in Figure 15. The uniaxial measurements were performed at a single frequency of 1 kHz. Cement mortar samples were cast in cubic molds, demolded after 1 day and cured in water for 7 or 28 days. Three samples per mix design were tested and the average was taken to be the representative value. The mixing protocol was the same as that for preparing the compressive strength samples.

After wet curing for the targeted duration the samples were air dried for 24 hours prior to testing. During drying, water can leave the pore structure. An open microstructure will experience high moisture loss, while a highly percolated mirostructure will experience limited moisture loss. As water is highly conductive compared to cement matrices, which is inherently insulating, low resistivity is associated with a more percolated microstructure, i.e. low permeability, and vice versa.

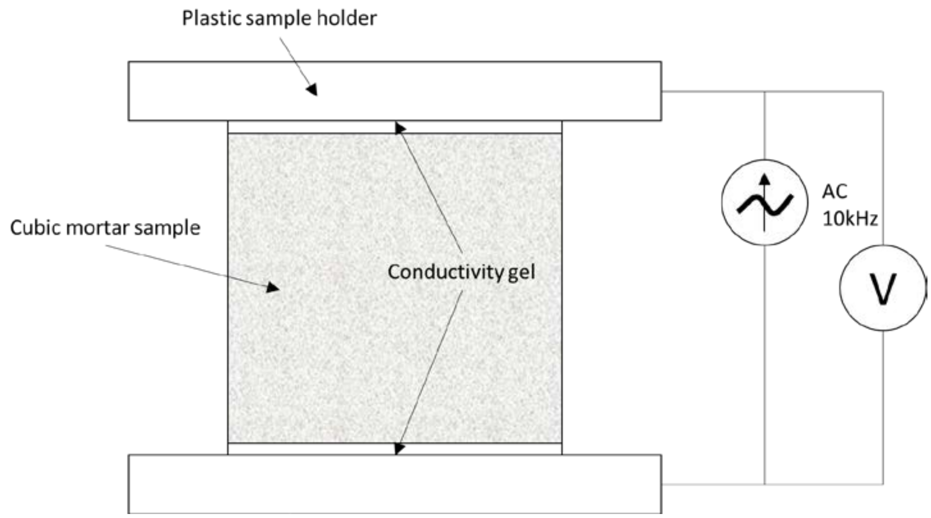


Figure 15 - Schematic of electrical resistivity meter.

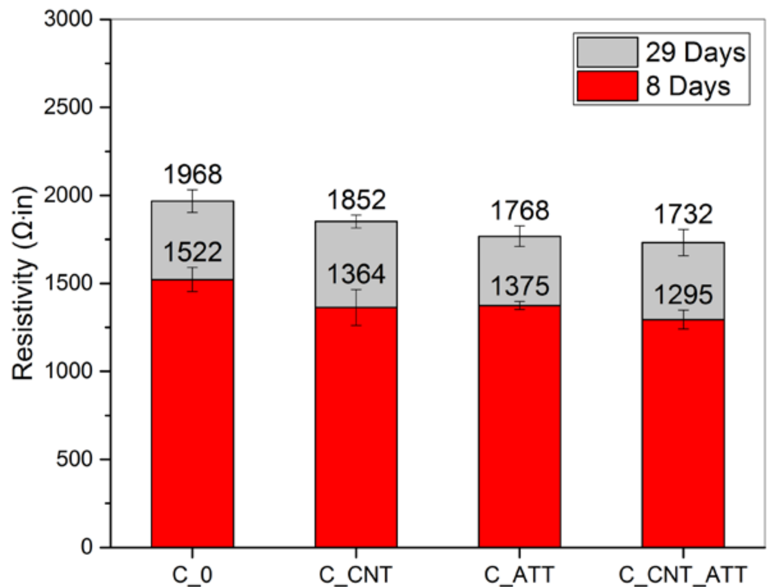


Figure 16 - Electrical resistivity of cement mortar systems.

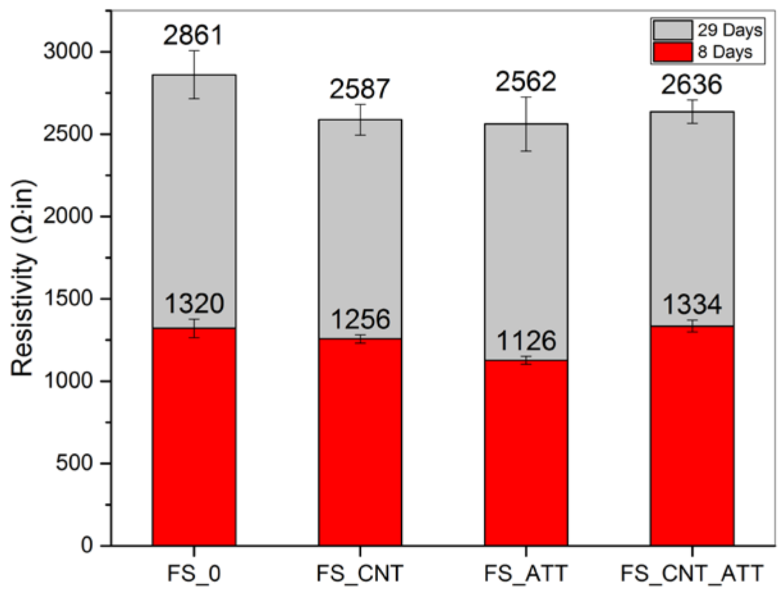


Figure 17 - Electrical resistivity of cement-fly ash-slag ternary mortar systems.

The results of electrical resistivity in the cement system and ternary system are shown in Figure 16 and Figure 17, respectively. Electrical properties depend on a number of factors, including the composition of the binder phases, therefore the results between the cement mortar system and ternary mortar systems can not be directly compared. However, the effect of the attapulgite clay and CNTs within each system can. The use of attapulgite clay and CNTs each led to slight decreases in resistivity in both systems, indicating higher percolation. In fact, the compressive strength results and electrical conductivity results were found to agree well. Comparing Figure 6 with Figure 16, and Figure 7 with Figure 17, it is apparent that they exhibit similar trends – increase in strength with decrease in resistivity and vice versa. This is reasonable, as a finer pore structure can enhance strength, along with reducing permeability. However, according to these resutlts, substantial changes to the permeability were not achieved with either CNTs or attapulgite.

3.3 SUMMARY

In summary, although the attapulgite clays were introduced into the mix design to control rheology, they were found to enhance the mechanical and transport properties, as well. Compared to CNTs, they had a comparable or greater effect. This can be attributed to improved dispersion of the ATT clays compared to the CNTs, and improved stability of the cement-based suspension.

4 RHEOLOGICAL CHARACTERIZATION

The rheological properties of fresh concrete mixes are important for processing. A balance between high flowability during casting and high stiffening upon placement is desired for coating applications. Therefore, steady-state flow properties, i.e. yield stress and viscosity, and static cohesion were measured.

All rheological characterization was performed on a HAAKE MARS III Rotational Rheometer, shown in Figure 18. And the chosen geometry was parallel-plate, as shown in Figure 19. The top plate had a diameter of 50 mm and the bottom plate was temperature-controlled with a circulating water bath set at 25°C. Both surfaces were covered with 120-grit adhesive sandpaper to prevent slip. Fresh mortar samples were placed on the bottom plate and the top plate was moved down to sandwich the sample until the targeted initial gap thickness of 4 mm was reached. Once the top plate was in position the sample was trimmed to match the diameter of the plate. Then, the rheological test was started. Three samples per mix design were tested and the average was taken to be the representative value.

Mortar samples were prepared by hand using the following mixing protocol:

1. Binder materials (i.e. cement, fly ash and/or slag) and sand were dry mixed for 1 min by hand.
2. CNTs were added as a suspension with a portion of the mixing water, then mixed for 3 min by hand.
3. Attapulgite nanoclays were added as a suspension with the remaining mixing water, then mixed for 3 min by hand.

For mixes without CNTs or nanoclays, only Steps 1 and 4 were performed. When only CNT or nanoclay was added, Step 2 or 3 was performed and all of the mixing water was added with the respective suspension. Fresh mortars were loaded into the rheometer immediately after mixing for testing.

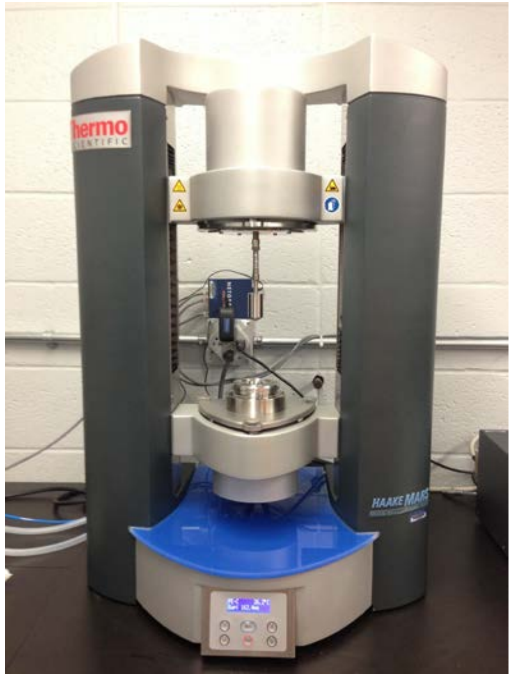


Figure 18 - Rotational rheometer.

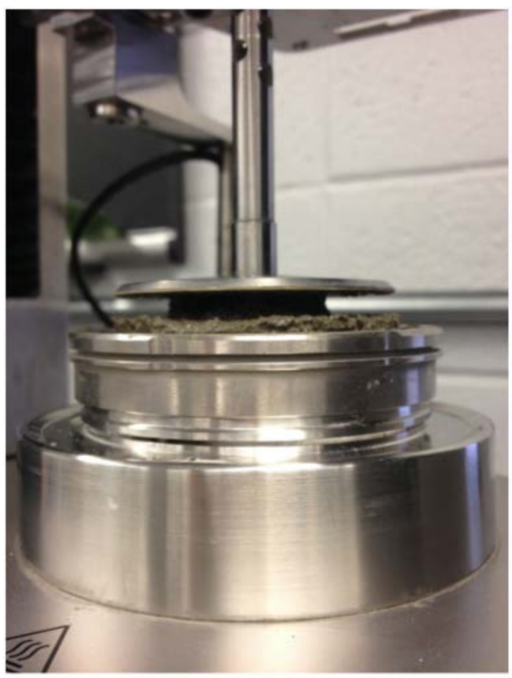


Figure 19 - Parallel-plate setup.

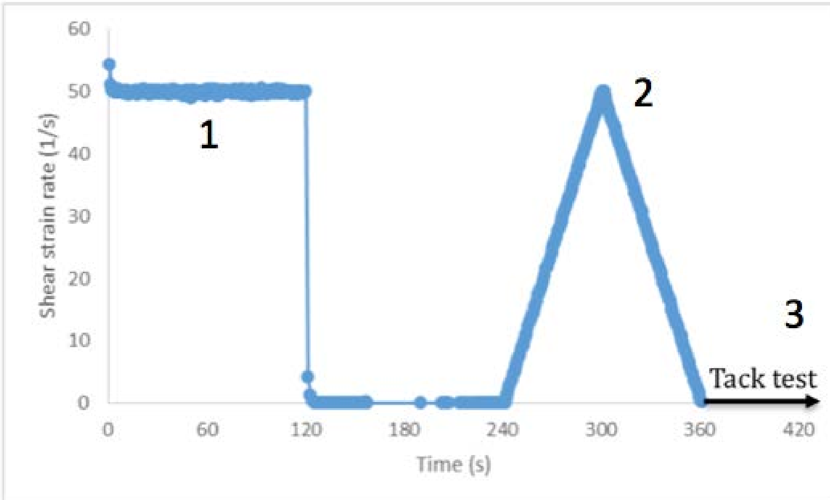


Figure 20 - Rheological protocol.

The applied rheological protocol is shown in Figure 20, from which steady-state properties and adhesive properties were obtained during each test run. The steps of the protocol and the obtained rheological parameters are discussed herein. The steps refer to the numbers in Figure 20.

STEP 1: Apparent viscosity

The sample was first subjected to a rate-controlled preshear of 50 1/s for 2 min, during which apparent viscosity was obtained. Viscosity is the resistance of the material to flow. A representative result is shown in Figure 21. The steady-state viscosity is taken to be the final apparent viscosity. Then the sample was allowed to rest for 2 min to undergo stress relaxation before the next step.

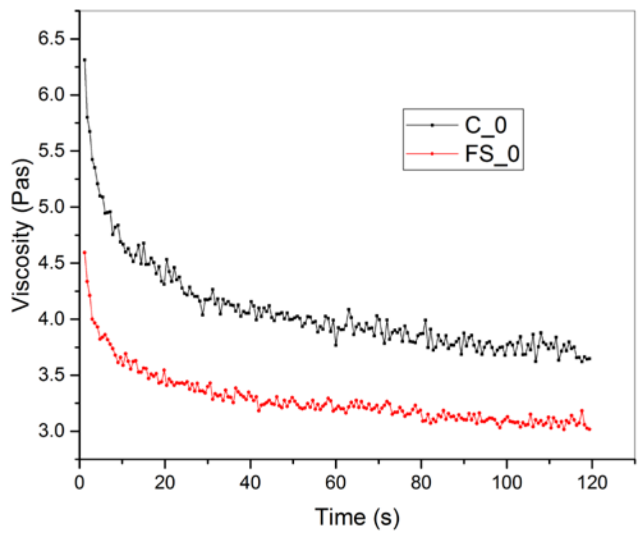


Figure 21 - Viscosity evolution obtained during preshear.

STEP 2: Yield stress

A linear ramp up and down was applied, from 0 1/s to 50 1/s back to 0 1/s over 120 s, during which the flow curve was obtained. The flow curve can be fitted with a Bingham model to obtain flow parameters – plastic viscosity and yield stress – as shown in Figure 22. A representative flow curve is presented in Figure 23, with a representation of the Bingham fitting on the downward portion of the curve. Since steady-state apparent viscosity is obtained in Step 1, only yield stress will be obtained here. Yield stress is the stress needed to initiate or terminate flow.

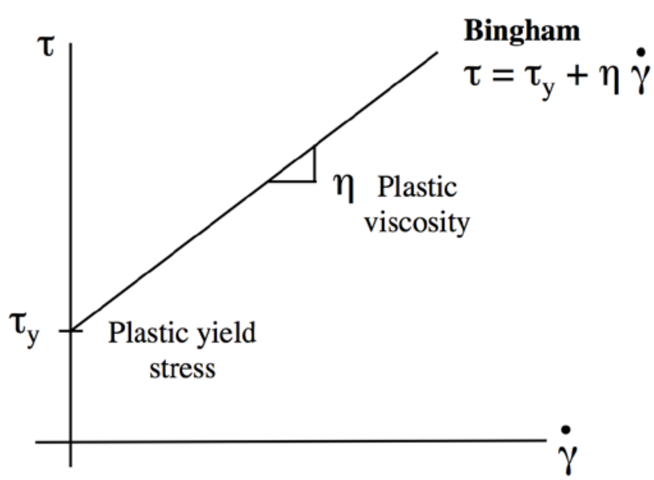


Figure 22 - Bingham model.

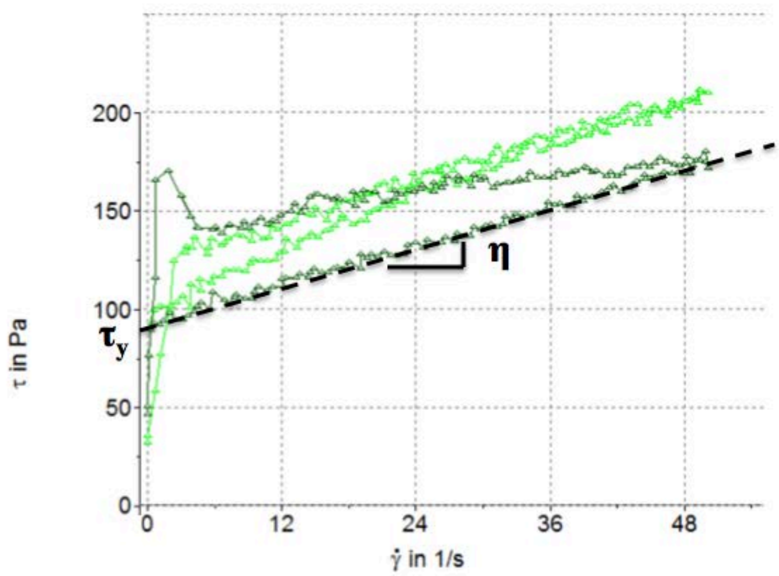


Figure 23 - Flow curve fitted with Bingham model to obtain yield stress and viscosity.

STEP 3: Static cohesion

Finally, after the linear up and down ramp, the tack test was performed. During this step, instead of applying a shear to the sample, the top plate was vertically moved upward at a constant velocity (10 μm/s) to subject the sample to stretching and the normal force was recorded. Figure 24 shows a schematic of the results. The peak marks the adhesive force, which is due to viscous dissipation and static cohesion. Then the material undergoes failure – either cohesive failure (within the material) or adhesive failure (at the material-plate interface). At relatively low plate velocities, viscous dissipation can be assumed to be low and the adhesive force can be considered to be primarily a measure of static cohesion.

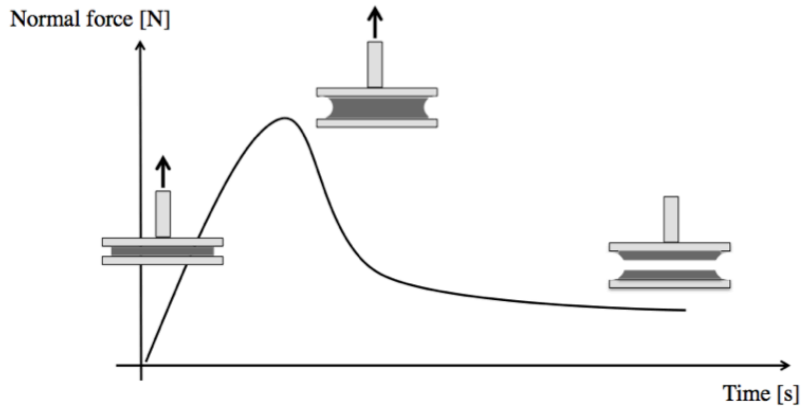


Figure 24 - Tack test results.

4.1 STEADY-STATE PROPERTIES RESULTS

4.1.1 APPARENT VISCOSITY

Figure 25 shows the results of viscosity, which is a measure of the resistance of the material under flow. Results indicate that the attapulgite clay had little to no effect on the viscosity in cement mortar – average values of 3.69 Pa-s and 3.59 Pa-s for mortars with 0% and 0.3% clay, respectively. And in the ternary cement-fly ash-slag mortar, the clays decreased viscosity by 13%. For the purpose of casting, it is desirable to keep it relatively low. Therefore the effect of the attapulgite clays on viscosity can be considered to be positive.

CNTs, on the other hand, had opposing effects between the two systems – they increased viscosity by 17% in the cement system and decreased it by 16% in the ternary system. This can be attributed to surfactant adsorption and admixture interactions, respectively. The surfactant used to disperse the CNTs is a polycarboxylate superplasticizer – a polymer with a backbone that is designed to adsorb onto the calcium sites of cement particles and side chains that are designed to repel cement particles from each other through steric hindrance. The surfactant adsorbs onto the CNTs, as well. Therefore, in the cement mortar with CNTs there is less surfactant available to disperse the cement particles, leading to higher viscosity. The same trend was not observed in the ternary system. The exact mechanisms are unknown but likely tied to increased complexity of interactions between the various constituents. More investigation is needed to elucidate. The combined addition of CNT and clay had opposing effects, as well, and can be explained in a similar manner.

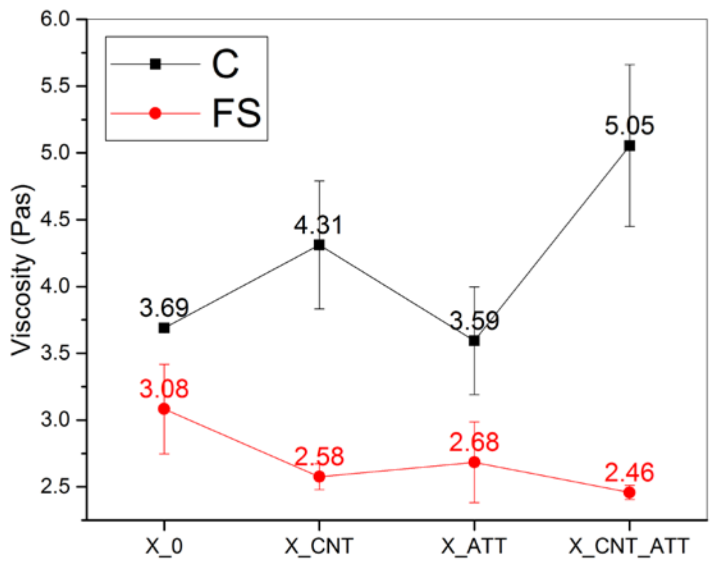


Figure 25 - Apparent viscosity.

4.1.2 YIELD STRESS

Figure 26 shows the results of yield stress, which is the stress needed to terminate or initiate flow. For placement on pipelines, it is desirable to keep it relatively high so the material stays on the target surface, given there is sufficient adherence or bonding. Yield stress increases with the attapulgite clay, where it is more pronounced in the cement mortar than in the ternary mortar – 80% versus 30%, respectively. Possible mechanisms include capillary suction, hydration mechanisms, water adsorption, particle packing and flocculation. A series of studies on the clay, which implemented rheological and imaging techniques, have demonstrated that increase in flocculation is the governing mechanism. The effect of the CNTs on yield stress, similar to viscosity, is opposing between the two systems – 28% increase in cement mortar and 10% decrease in ternary mortar. This is again likely tied to dispersion issues and admixture interaction.

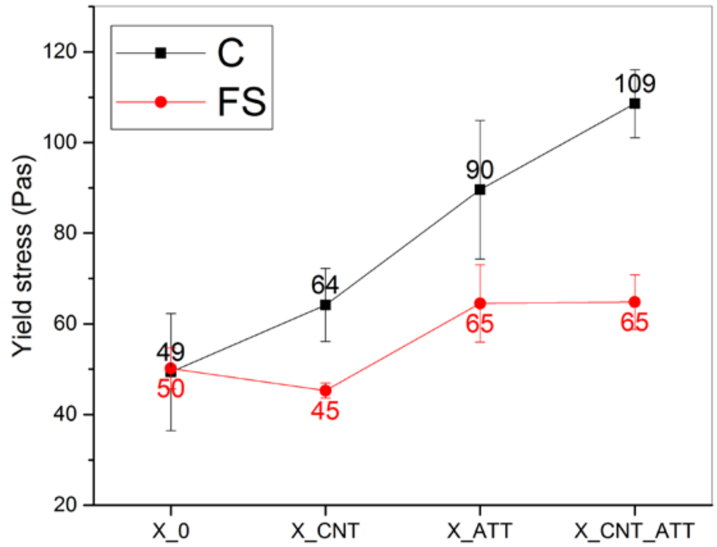


Figure 26 - Yield stress.

4.2 TACK TEST RESULTS

Static cohesion was also characterized and the results are presented in Figure 27. Cohesion is closely tied to yield stress. Comparing the two results, Figure 26 and Figure 27, they are found to exhibit similar trends. The clays enhance cohesion in both systems – 31% and 27% in cement and ternary, respectively. And the CNTs have opposing effects – 20% increase in cement mortar and 11% decrease in ternary mortar.

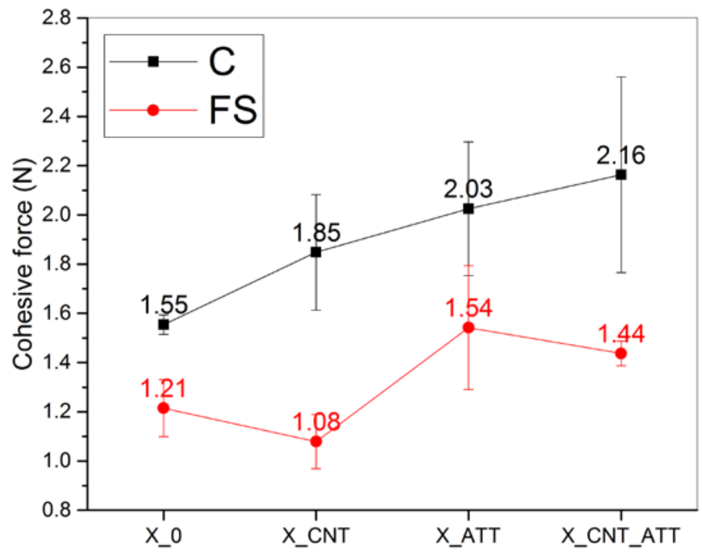


Figure 27 - Static cohesion.

4.3 SUMMARY

In summary, the clays were demonstrated to be effective in balancing low viscosity and high static yield stress and cohesion. This balance is desirable for processing of pipeline coatings. The material can exhibit high flowability during casting but high stiffening immediately upon placement onto the target surface. And opposing effects by the CNTs on the rheological parameters between the cement and cement-fly ash-slag systems were consistently captured. This has been linked to the increased complexity of admixture hahainteractions in ternary systems versus unitary systems.

5 CONCLUSIONS AND RECOMMENDATIONS

Replacement of cement content with SCMs by up to 50% while achieving comparable mechanical properties as the control was possible.

Results of the work indicate that although the nanoclays were utilized primarily as a rheological modifier, they had an enhancing effect on the mechanical properties that were comparable to or greater than the CNTs. This was attributed to improved suspension stability and seeding effects achieved through the nanoclays, and the difficulty in achieving effective dispersion of the CNTs.

Although the findings indicated that SCMs, CNTs, and attapulgite clays were found to improve permeability, the effect was not significant. Therefore, cement-based coatings as a stand alone solution for pipelines is likely not feasible and instead requires a dual layer with a polymer-based base coating.

Rheological characterization indicated that the attapulgite clays exhibited a balance between high flowability during casting and high stiffening at rest that would be beneficial for the process of coating.

Enhancement in rheology in combination with the improvement in mechanical properties and permeability suggests that attapulgite clays may be sufficient for pipeline coatings, not requiring CNTs. This can be beneficial as this simplies the system to avoid complex admixture interactions and incompabilities. Further, attapulgite clays are readily dispersible, making processing less costly and more efficient.

A summary of the key results are presented in Table 3.

Table 3 - Comparison of the effects of attapulgite clays and CNTs on mechanical, hardening and rheological properties

Testing methods	Attapulgite Clay		CNT		Summary
	Cement	Ternary	Cement	Ternary	
Compressive strength	↑	↑	↑	–	Attapulgite clays introduce enhancing effects on mechanical and hardening properties that are comparable to or greater than those by CNTs.
Tensile strength	↑↑↑	–	–	↑↑	
Isothermal calorimetry	↑		–		
Permeability	↓	↓	–	↓	CNTs and attapulgite clays can reduce permeability, but results indicate that the degree is moderate.
Apparent viscosity	–	↓	↑	↓	The effect of attapulgite clays on rheology is positive, as it is desirable to keep viscosity low during casting and static yield stress and cohesion high after placement.
Yield stress	↑↑↑↑↑↑↑↑	↑↑↑	↑↑↑	–	
Cohesion	↑↑↑	↑↑	↑↑	–	

*Note: − : <10%; ↑ : 10%-20%; ↑↑:20%-30%; ..... ↑↑↑↑↑↑↑↑: 80%-90%